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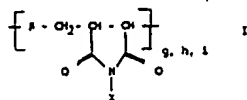
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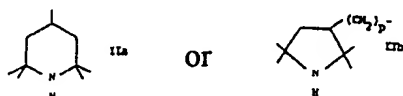
(54) Oligomeric and Polymeric Compounds, Their Preparation and Their Use as Light Stabilizers for Plastics, Especially for Polypropylene

(57) Oligomeric and polymeric compounds which consist of copolymers A_g, B_h and C_i with repeat units according to the formula



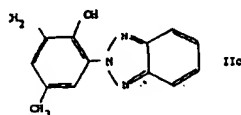
in which X denotes:

a) in copolymer A_g a radical according to the formula



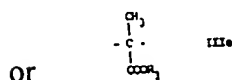
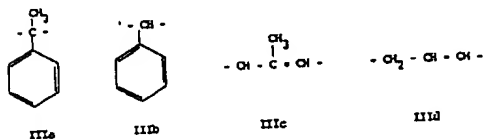
in which p denotes an integer ranging from 0 to 2,

b) in copolymer B_h a radical according to the formula



and

c) in copolymer C_i a (C₁₀-C₃₀) alkyl radical, and g, h and i may be identical or different and denote a number of 0-25, wherein the sum of g, h and i must be at least 2, and R denotes a radical according to the formula



in which R₁ is a (C₁-C₁₄) alkyl radical, a process for preparing same and their use as light stabilizers.

The following data were taken from the documents submitted by the applicant

Specification

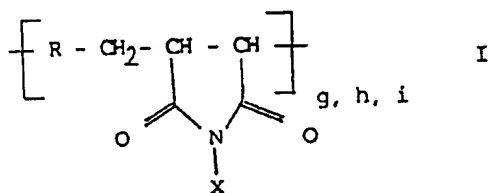
Monomeric acrylic acid derivatives which contain at least one piperidinyl group with a sterically hindered nitrogen atom and are used as light stabilizers in organic polymers are described in US 3,705,166. However, these compounds have the drawback that they are highly volatile and can be easily extracted with water or other liquids and that they interfere with the polymer structure on incorporation in the polymer, as a result of which the properties of the polymer are altered.

Polymeric light stabilizers have already been known from the literature. For example, high polymeric 2-hydroxy-4-acryloyloxybenzophenone derivatives are used in US 3,365,421. Copolymeric light stabilizers which can carry piperidinyl, benzophenone or benzotriazole radicals are described, e.g., in EP-A 0 010 518.

The object of the present invention was to find new oligomeric and polymeric compounds which possess improved properties compared with the state of the art, such as better compatibility in plastics, and lead to a substantially increased UV stability in the plastics to be protected.

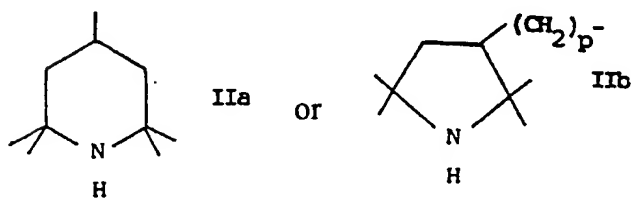
It has now been found that this object can be accomplished by means of copolymers which contain maleimide *N*-hydroxyphenylbenzotriazole units and/or maleimide *N*-tetramethyl piperidinyl or pyrrolidinyl units, optionally combined with maleimide *N*-alkylene units.

Consequently, the present invention pertains to oligomeric and polymeric compounds which are characterized in that they consist of copolymers A_g , B_h and C_i with repeat units according to the formula



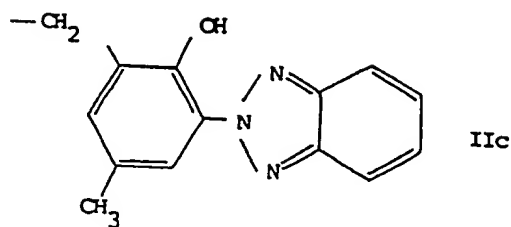
in which X denotes:

a) in copolymer A_g a radical according to the formula



in which p is a number ranging from 0 to 2,

b) in copolymer B_h a radical according to the formula

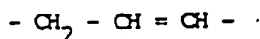
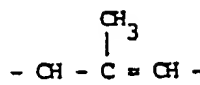
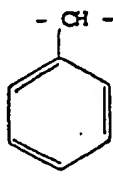
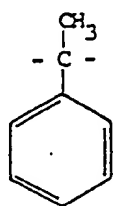


and

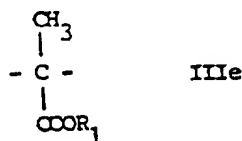
c) in copolymer C_i a (C₁₀-C₃₀) alkyl unit,

g, h and i may be a number of 0-25, wherein the sum of g, h and i must be at least 2, and

R denotes a radical according to the formula



or



in which R₁ may be a (C₁-C₁₄) alkyl radical.

The compounds according to the present invention are synthesized from the copolymers A_g, B_h and C_i, which have the basic structure according to formula I each, wherein the substituent X varies. In copolymer A_g, X denotes a tetramethyl piperidiny radical according to formula IIa or a tetramethyl pyrrolidiny radical according to formula IIb, in which p is a number ranging from 0 to 2. X in A_g preferably denotes a radical according to formula IIa.

In copolymer B_h, X denotes a benzotriazole radical according to formula IIc. In copolymer C_i, X denotes a (C₁₀-C₃₀) alkyl radical, which may be linear or branched, such as a decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, tetracosyl or triacontyl radical.

R denotes in all copolymers a radical according to formulas IIIa through IIIe, in which R₁ may be a branched or linear (C₁-C₁₄) alkyl radical, preferably a (C₁-C₆) alkyl radical, such as a methyl, ethyl, *iso*-propyl, *n*-propyl, butyl, *tert*.-butyl, hexyl, decyl or tetradecyl radical. R preferably denotes the radical according to formula IIIa or IIIe.

The subscripts g, h and i may be identical or different and denote a number ranging from 0 to 25, and the sum of g, h and i must be at least 2.

A preferred embodiment of the compounds according to the present invention is a three-block copolymer, consisting of a combination of the three copolymers A_g , B_h and C_i , wherein the subscripts g , h and i may be identical or different and denote a number ranging from 1 to 25.

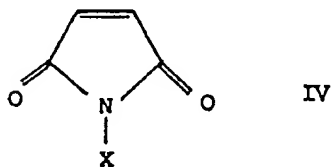
Other preferred embodiments of the compounds according to the present invention are two-block copolymers which consist of combinations of the copolymers

- a) A_g and B_h
- b) A_g and C_i and
- c) B_h and C_i

in which the subscript of the particular missing copolymer equals 0 and the other two subscripts are identical or different and denote a number ranging from 1 to 25.

Furthermore, oligomeric compounds are preferred which consist a) of copolymer A_g only or b) of the copolymer B_h only, wherein g and h denote a number ranging from 2 to 10 and i equals 0.

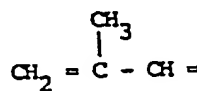
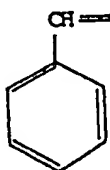
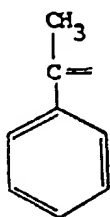
The present invention also pertains to a process for preparing the above-described compounds, which is characterized in that one of the copolymers A_g , B_h or C_i is prepared in the first step by the polymerization of an equimolar mixture of a maleimide according to the formula



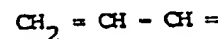
in which X has the meaning a), b) or c) corresponding to the particular copolymer as defined above, and a comonomer according to the formula



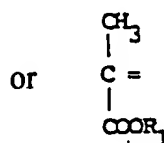
in which R' denotes a radical according to the formula



Vc



Vd



Ve

and the copolymer thus obtained is optionally subjected to further polymerization in the second step to obtain one of the two-block copolymers A_g-B_h , A_g-C_i or B_h-C_i by adding an equimolar mixture of a maleimide according to formula IV, in which X has the corresponding meaning a), b) or c) as defined above, of the second copolymer, and a comonomer according to formula V, in which R' has the meaning defined above, after which the two-block copolymer thus obtained is optionally polymerized in a third step to obtain a three-block copolymer by adding an equimolar mixture of a maleimide according to formula IV, in which X has the meaning a), b) or c) as defined above, of the third copolymer and a comonomer according to formula V, in which R' has the meaning defined above.

In formula IV, X has the meaning given above for the copolymers A_g , B_h and C_i .

Maleimides according to formula IV are therefore 2,2,6,6-tetramethyl-4'-piperidiny-*N*-maleimide-3-maleimido, 2,2,5,5-tetramethyl-1-pyrrolidiny, 2-(2'-hydroxy-4'-methylenemaleimide-5'-methylphenol)-benzotriazole and maleimide-*N*-(C_{10} - C_{30}) alkyls.

The comonomers according to formula V are α -methyl styrene, styrene, isoprene, butadiene or a methacrylic acid (C_1 - C_{14}) alkyl ester. The preferred comonomers are α -methyl styrene and methacrylic acid (C_1 - C_4) alkyl esters, such as methacrylic acid methyl, ethyl, propyl or butyl ester.

Free radical and ionic copolymerization are suitable for preparing the compounds according to the present invention. The molecular weight can be controlled, e.g., by means of initiators, regulators or free radical chain terminators. The polymerization may be carried out in substance, in solution, in dispersion, in emulsion or in suspension, depending on the starting compounds selected.

The ionic and free radical polymerization in solution is preferably used to prepare the compounds according to the present invention.

The preparation of the compounds according to the present invention begins, for example, in the case of one of the copolymers A_g , B_h or C_i , e.g., with the stoichiometric polymerization of 2-(2'-hydroxy-4'-methylenemaleimide-5'-methylphenol)-benzotriazole (HMB) with a comonomer at a molar ratio of 1:1.

The polymerization is preferably carried out in solvents and diluents which are inert under the reaction conditions, such as toluene, dioxane, acetone, benzene or tetrahydrofuran.

An initiator, preferably an organometallic initiator, e.g., naphthalene sodium, diisobutyl tin, *n*-butyl lithium or triethyl aluminum, used in catalytic quantities, is preferably added to the reaction mixture for the ionic polymerization. The length of the polymer chain can be set by selecting the ratio of the monomer to the initiator. The catalysts suitable for the free radical polymerization include, e.g., *tert*.-butyl(2,2-dimethylpropanoyl) peroxide and *tert*.-butyl peroxopivalate or *tert*.-butyl peroxyisobutyrate, *tert*.-butyl peroxyneodecanoate, *tert*.-amyl peroxyneodecanoate, and *tert*.-amyl peroxyneodecanoate. The amount of the monomers used depends on the desired total molecular weight of the compound. The temperature during the polymerization may vary depending on the starting compounds and the polymerization techniques used and is approximately between 0°C and 80°C. The polymerization time is about 15 to 200 minutes.

If the compound according to the present invention consists of two copolymers, an equimolar mixture of, e.g., 2,2,6,6-tetramethylpiperidiny-*N*-maleimide (TPM) or 3-maleimido-2,2,5,5-tetramethyl-1-pyrrolidiny (3-MTP) is subsequently allowed to flow in with one of the above-mentioned comonomers.

The temperature is again about 0°C to 80°C, and the polymerization time is about 15 to 200 minutes.

If the compound according to the present invention consists of the copolymers A_g, B_h and C_i, the last step is repeated with a mixture of a maleimide-*N*-(C₁₀-C₃₀) alkyl (AM) with one of the above-mentioned comonomers. Identical comonomers are preferably used for the different copolymers A_g-B_h and C_i during the preparation of the compounds according to the present invention.

The order of the copolymers A_g, B_h and C_i during the preparation of two-block and three-block polymers may be selected freely. The polymerization may also be carried out under an inert gas atmosphere, e.g., under a nitrogen atmosphere.

The compounds thus prepared are preferably isolated by concentration by evaporation or by precipitation in *n*-hexane or water, or by extraction, e.g., with diethyl ether.

The total molecular weight of the compounds according to the present invention is between about 500 and 10,000 g/mole and preferably 1,000 to 8,000 g/mole, depending on the desired application.

The preparation of the monomers TPM and 3-MTP used to prepare the copolymer A_g may be carried out, e.g., analogously to EP 0 000 496.

The monomer of copolymer B_h, HMB, is novel and consequently another subject of the present invention. It is prepared by reacting hydroxymethylene-*N*-maleimide and 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole while water is eliminated.

The monomer of the copolymer C_i, AM, is prepared, e.g., by reacting maleic anhydride with a longer-chain aminoalkyl.

The compounds according to the present invention are suitable for use as light stabilizers for plastics. The present invention consequently also pertains to the use of the compounds according to the present invention as light stabilizers for plastics. They are added to the plastics to be protected at a concentration of about 0.05 wt. % to 5 wt. % relative to the plastic. The amounts preferably added are about 0.1 wt. % to 2.5 wt. % of light stabilizer.

The incorporation in the plastic may be carried out after the polymerization, e.g., by mixing the light stabilizers and optionally additional additives into the plastic melt before or during the shaping, or by applying the dissolved or dispersed compounds to the plastic, optionally with subsequent evaporation of the solvent. Besides the light stabilizers according to the present invention, additional additives may be added to the plastics to be protected. Such additives are, e.g., antioxidants, plasticizing agents, lubricants, emulsifying agents, fillers, glass fibers, flameproofing agents, pigments, antistatics, etc.

The compounds according to the present invention are particularly compatible with plastics such as polyolefins, styrene polymers, polyamides and polyurethanes. They are preferably used in polyolefins, such as polyethylene or polypropylene, and especially preferably in polypropylene.

Furthermore, the compounds according to the present invention are characterized by a markedly improved stability of the plastics compounded with them compared with the state of the art. The plastics treated with the compounds according to the present invention as light stabilizers are suitable for preparing paints, films, plates, fibers, injection moldings or films.

Example 1

Preparation of 2,2,6,6-Tetramethyl-4-piperidinyl N-Maleimide

31.3 g (0.35 moles) of maleic acid anhydride (MAA), dissolved in 50 mL of dimethylformamide (DMF), were charged in advance into a heatable three-necked flask equipped with a reflux cooler, a stirrer, a thermometer and a feed unit.

Then, 70.5 g (0.30 moles) of tetramethyl piperidinylamine in 50 mL of DMF were added dropwise at room temperature, while the amido acid precipitated. Then, 0.2 g of potassium acetate, 50 g (0.35 moles) of acetic anhydride and 3.5 g (0.06 moles) of triethylamine were added to the reaction mixture.

The reaction mixture was heated at 50°C for 60 minutes and subsequently added dropwise to 200 g of ice water, after which the reaction product precipitated. The reaction product was filtered off on a sintered-glass filter, washed with water, and dried.

Yield: 68 g (83%)

Melting point: Approx. 95°C.

Example 2

Preparation of N-Stearyl Maleimide

31.3 g of MAA were dissolved in 50 mL of DMF and charged in advance into the apparatus described in Example 1. At room temperature, 80.85 g (0.30 moles) of 1-octadecylamine in 50 mL of DMF were added dropwise, and the amido acid precipitated. Then, 0.2 g of cobalt acetate, 50 g (0.35 moles) of acetic anhydride and 3.5 g (0.06 moles) of triethylamine were added, and the reaction mixture was maintained at 50°C for one hour.

The reaction mixture was precipitated in 200 g of ice water, filtered off on a sintered-glass filter, washed with water, and dried.

Yield: 111 g (91%)

Melting point: Approx. 85°C.

Example 3
Preparation of 2-(2'-Hydroxy-4'-methylenemaleimide-5'-methylphenol) Benzotriazole

8.0 g (63 moles) of hydroxymethylene-*N*-maleimide were reacted with 15.6 g (69 mmoles) of 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole in 50 g of concentrated sulfuric acid (97%). To do so, the reaction mixture was first cooled with ice for 2 hours and the temperature was then slowly raised to room temperature. After a total of 20 hours, the reaction mixture was poured into cold water and the precipitate thus formed was filtered off, washed, and dried.

The crude product was subsequently recrystallized from ethanol-ethyl acetate (1:1) and dried under vacuum.

Yield: 18.9 g (90%).

Melting point: 203-205°C.

Example 4
Preparation of a Two-Block Copolymer A_g-B_h

45.4 g of 2-(2-hydroxy-4-methylenemaleimide-5'-methylphenol) benzotriazole were copolymerized with 11.8 g of α -methyl styrene at a molar ratio of 1:1 in 200 mL of toluene. The reaction temperature was 0°C. Naphthalene sodium was added as the initiator in an amount of 0.5 g. After 30 minutes, an equimolar mixture of 11.8 g of α -methyl styrene and 23.6 g of 2,2,6,6-tetramethyl-4-piperidiny-*N*-maleimide in toluene was allowed to flow at 0°C.

The polymer thus prepared was isolated from the solution after 15 minutes by concentration by evaporation.

The molecular weight was 5,000 g/mole.

Example 5
Preparation of an Alternating Copolymer B_h

A 30% solution of equimolar quantities of 2-(2'-hydroxy-4'-methylenemaleimide-5-methylphenol) benzotriazole and styrene was prepared in acetone. Then, 0.158 wt.% of *tert.*-butyl(2,2-dimethylpropanoyl) peroxide were added relative to the monomer mixture and the batch was maintained at a temperature below 20°C.

The solution was pumped continuously for 3 hours in a tank heated to 60°C, which already contained acetone.

The tank was equipped with a stirrer, a reflux cooler and a nitrogen inlet tube. After the end of the polymerization, water was added in an excess amount while stirring vigorously, while the polymer precipitated. The solvent was removed by stripping with steam. The copolymer was then filtered and dried. The yield was 90%, and the melting point of the polymer was 180°C to 200°C.

Example 6

Preparation of a Two-Block Copolymer A_g-B_h

5 The alternating copolymer thus obtained in Example 5 was dissolved in benzene in a tank equipped with a temperature indicator, reflux cooler, stirrer and a nitrogen inlet tube, and the temperature was maintained at 60°C.

10 The necessary amounts of styrene and 2,2,6,6-tetramethyl-4-piperidiny-*N*-maleimide were added under nitrogen and the entire batch was stirred for 3 hours. *tert.*-Butyl peroxyvalate (75%) in hexane was also added as a catalyst in some cases.

15 After a reaction time of 2 hours, the benzene-insoluble fraction was separated by precipitation in benzene. The benzene-insoluble fraction yielded the grafted block copolymer after extraction with diethyl ether.

Example 7

Preparation of a Three-Block Copolymer $A_g-B_h-C_i$

20 The two-block copolymer thus obtained in Example 6 was dissolved in benzene in a tank equipped with a temperature indicator, a stirrer and a nitrogen inlet tube, and the temperature was maintained at 60°C.

25 The necessary amounts of styrene and *N*-stearyl maleimide were added under nitrogen and the entire batch was stirred for 3 hours. *tert.*-Butyl peroxyvalate (75%) in hexane was also added as a catalyst in some cases.

30 After a reaction time of 2 hours, the benzene-insoluble fraction was separated by precipitation in benzene. The benzene-insoluble fraction yielded the grafted block copolymer after extraction with diethyl ether.

Other two-block copolymers and three-block copolymers were prepared analogously to Example 6 and Example 7 with the amounts indicated in Table 1.

35 All compounds prepared had a glass transition temperature around 100°C and a molecular weight of about 5,000 g/mole.

Table 1

Ex.	Copoly- meric B _h (g)	Styrene (g)	TPM (g)	3-MTP (g)	SM (g)	Benzene (mL)	Temp. (°C)	Time (min.)	Conversion (%)
5	8	20	10.4	35.4	-	30	80	120	80
	9	20	10.4	-	34.9	30	80	120	90
10	10	20	10.4	-	22.1	30	80	120	95

b) Three-block copolymers

Ex.	Two-block copolymer from	Styrene (g)	SM (g)	3-MTP (g)	Benzene (mL)	Temperature (°C)	Time (min.)	Conversion (%)	
15	Ex. #/(g)								
20	11	6/20	10.4	34.9	-	30	80	120	95
	12	9/20	10.4	-	22.1	30	80	120	80
	13	10/20	10.4	34.9	-	30	80	120	85
SM	N-Stearyl maleimide								

Example 8

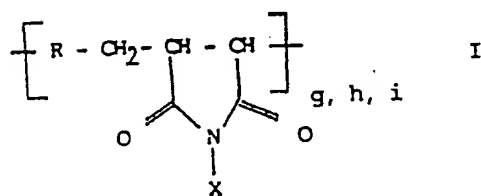
A polymer prepared according to Example 4 was incorporated in amounts of 0.1 wt.%, 0.3 wt.%, 0.5 wt.% and 1 wt.% in Daplen FM 55. Film strips of a thickness of 30 μm were prepared and their strength was tested by the Xenon Test 150 after increasing exposure time. The corresponding times after which the tear strength was reduced to 50% were measured and the results are shown in Table 2.

Table 2

Concentration (wt. %)	Time (hours)
0.1	2,000
0.2	5,000
0.3	6,000
0.5	8,000
1.0	15,000

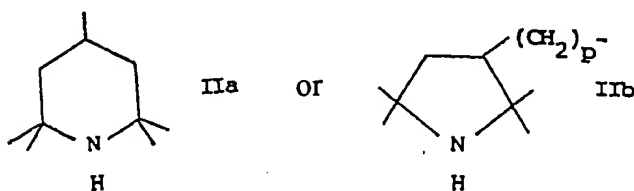
Patent Claims

1. Oligomeric and polymeric compounds, characterized in that they consist of copolymers A_g , B_h and C_i with repeat units according to the formula



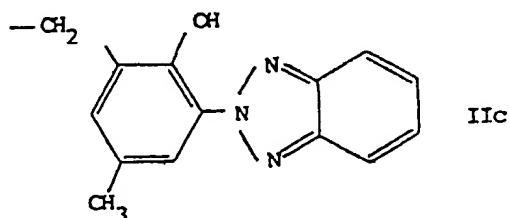
in which X denotes:

a) in copolymer A_g a radical according to the formula



in which p denotes a number ranging from 0 to 2,

b) in copolymer B_h a radical according to the formula

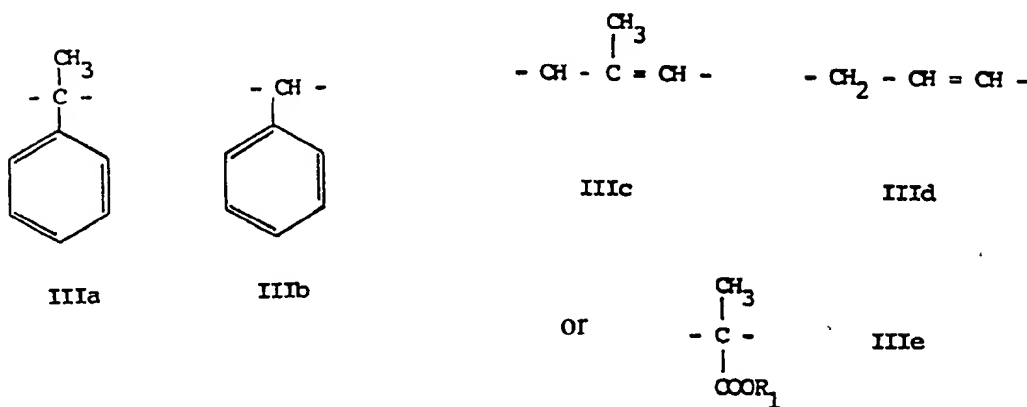


and

c) in copolymer C_i a (C_{10} - C_{30}) alkyl radical,

g, h and i may be identical or different and denote a number of 0-25, wherein the sum of g, h and i must be at least 2,

and R denotes a radical according to the formula



wherein R_1 denotes a (C_1 - C_{14}) alkyl radical.

2. Compounds in accordance with claim 1, characterized in that they are three-block copolymers, consisting of the copolymers A_g , B_h , C_i with repeat units according to formula I, in which g, h and i are identical or different and denote a number ranging from 1 to 25, and X and R are defined as in claim 1.

3. Compounds in accordance with claim 1, characterized in that they are two-block copolymers, consisting of the copolymers A_g and B_h with repeat units according to formula I, in which g and h are identical or different and denote a number ranging from 1 to 25, i equals 0, and X and R are defined as in claim 1.

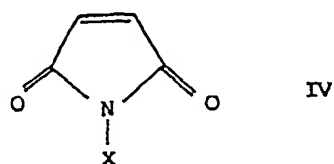
4. Compounds in accordance with claim 1, characterized in that they are two-block copolymers, consisting of the copolymers A_g and C_i with repeat units according to formula I, in which g and i are identical or different and denote a number ranging from 1 to 25 and h equals 0 and X and R are defined as in claim 1.

5. Compounds in accordance with claim 1, characterized in that they are two-block copolymers, consisting of the copolymers B_h and C_i with repeat units according to formula I, in which h and i are identical or different and denote a number ranging from 1 to 25 and g equals 0 and X and R are defined as in claim 1.

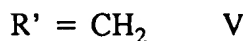
6. Compounds in accordance with claim 1, characterized in that they consist of a copolymer A_g with repeat units according to formula I, in which g is a number ranging from 2 to 10, h and i equal 0 and X and R are defined as in claim 1.

7. Compounds in accordance with claim 1, characterized in that they consist of a copolymer B_h with repeat units according to formula I, in which h is a number ranging from 2 to 10, g and i equal 0 and X and R are defined as in claim 1.

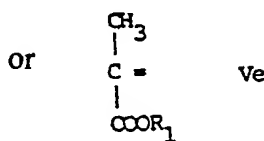
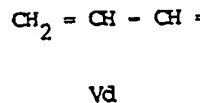
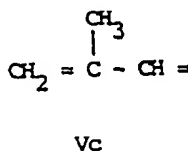
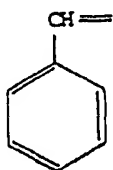
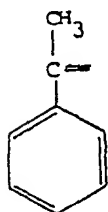
8. Process for preparing compounds in accordance with claim 1, characterized in that one of the copolymers A_g , B_h or C_i is prepared in the first step by the polymerization of an equimolar mixture of a maleimide according to the formula



in which X has the meaning a), b) or c) according to claim 1 corresponding to the particular copolymer, and a comonomer according to the formula



in which R' denotes a radical according to the formula



and the copolymer obtained is optionally subjected to further polymerization in the second step to obtain one of the two-block copolymers A_g-B_h , A_g-C_i or B_h-C_i by adding an equimolar mixture of a maleimide according to formula IV, in which X has the corresponding meaning a), b) or c) according to claim 1 of the second copolymer, and a comonomer according to formula V in which R' has the meaning defined above,

after which the two-block copolymer thus obtained is optionally polymerized in a third step to obtain a three-block copolymer by adding an equimolar mixture of a maleimide according to formula IV, in which X has the meaning a), b) or c) according to claim 1 of the third copolymer and a comonomer according to formula V, in which R' has the meaning defined above.

9. Use of compounds in accordance with claim 1 as light stabilizers for the UV stabilization of plastics, preferably polypropylene.

10. 2-(2'-Hydroxy-4'-methylenemaleimide-5'-methylphenyl) benzotriazole.

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